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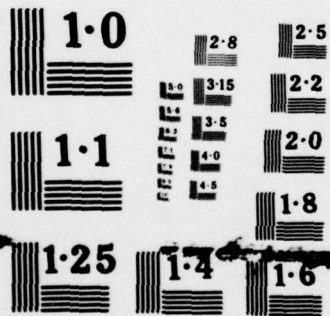
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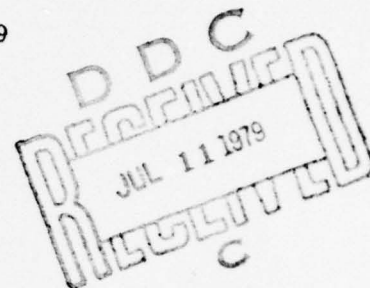
THE STUDY AND IDENTIFICATION OF RESIDUAL DONOR
SPECIES IN HIGH PURITY SEMICONDUCTORS

Final Report
for period 1 June 1978 to 31 May 1979

Contract No. N00173-78-C-0129

Prepared by

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INTRODUCTION

The purpose of this contract was to establish a facility for the study and identification of shallow donors and acceptors in high purity semiconductors. The use of Fourier transform spectroscopy to measure photothermal excited state photoconductivity is one of the most sensitive methods available for the study of shallow impurity states, and this final report describes the basic theory of the photothermal ionization technique and the current status of the facility. The research to be conducted on a new contract, N00173-79-C-0184, using this facility is briefly described.

The Fourier transform spectroscopy apparatus is operational, although further modification must be made to realize its full resolution and sensitivity. Interferogram data have been taken and low resolution Fourier transforms have been made for silicon samples in an attempt to optically detect the X-levels associated with indium and gallium. The photoconductivity signal of a GaAs sample well characterized by previous experiments at Lincoln Laboratory has been monitored to optimize the optics and improve the noise characteristics of the sample biasing electronics.

Basic Theory

For shallow impurities a simple hydrogenic model can be used to estimate the impurity energy levels. In this model, a donor atom, relative to the host atom it replaces, has one extra valence electron and one extra positive nuclear charge. This is analogous to a hydrogen atom in a vacuum. Using the dielectric constant and effective mass appropriate for the semiconductor (instead of for the vacuum) a model Hamiltonian for the impurity electron can be written:

$$H = \frac{-\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{\epsilon_0 r}$$

Except for the replacement of m by m^* and e^2 by $\frac{e^2}{\epsilon_0}$, this is the familiar Hamiltonian of the hydrogen atom. The replacements simply rescale the energy and distance scales of the hydrogenic solutions giving the energy and Bohr radius for the n^{th} state as

$$E_n = m^* e^4 / 2 \epsilon_0^2 \hbar^2 n^2 = 13.6 (m^*/m) / \epsilon_0^2 n^2 \text{ eV}$$

$$a_{Bn} = (\hbar^2 / m^* e^2) n^2 \epsilon_0 = 5.29 \times 10^{-9} n^2 \epsilon_0 / (m^*/m) \text{ cm}$$

where (m^*/m) is the effective mass ratio and ϵ_0 is the static dielectric constant of the semiconductor. It should be noted that the hydrogenic model predicts precisely the same energy level spectrum and wavefunctions for all donor species.

Although it is clear that the potential seen by the electron close to the donor atom will not be the simple coulomb potential of the model Hamiltonian, for shallow donor levels (large Bohr radii) this causes only a small perturbation on the hydrogenic energy spectrum, called alternately the central cell correction or chemical shift. This is because only a small fraction of order $(a_0/a_{B1})^3$ of the electron wavefunction overlaps the neighborhood of the donor atom where the potential is non-coulombic, where a_0 is a lattice constant. For different impurity species in GaAs, the sign of the corrections observed has always been the same, owing perhaps to the increased attraction felt by the electron when it penetrates the donor ion core. However, the magnitude of the correction depends on the details of the electronic structure of the donor in the lattice and is in general different for different impurity species. This species dependence of the central cell correction is the means through which impurities can be identified spectroscopically.

The ground state central cell corrections for several donor species in GaAs appear in Table I. Because of the similar ionization energy of shallow impurities in InP, the as yet unmeasured central cell corrections are expected to be comparable.

EXPERIMENTAL METHOD

A means by which these energy level spectra and the associated central cell corrections may be measured in high purity semiconductors is photothermal ionization spectroscopy. This is the most sensitive method for analysis of impurities in high purity semiconductors. Other methods such as optical absorption, radio chemistry, and mass spectrometry are inadequate to identify impurities at the extremely small concentrations present in high purity material.

The photothermal ionization technique is based on the fact that the extrinsic photoconductivity spectrum, under certain conditions, is a line spectrum which corresponds to the bound electron energy levels of the impurities. The techniques' sensitivity is due to the fact that the magnitude of the photoresponse does not decrease with decreasing impurity concentration down to very low concentrations. This is a consequence of the voltage sensitivity of the extrinsic photoconductivity being proportional to $\Delta n/n$, where n is the total carrier concentration without illumination and Δn is the change in carrier concentration under illumination. Both n and Δn depend in the same way on the concentration of major and compensating impurities and so this dependence cancels out of the voltage sensitivity. This feature of the method enables the detection and identification of impurity species even in concentrations so small that all other methods of analysis fail.

TABLE 1

Central Cell Corrections to the Parabolic Band Ry^* ($=46.10\text{cm}^{-1}$) for Four Residual Donors in High Purity GaAs^a

Donor	Central cell correction	Ionization energy ^{b,c}
1	0.064 meV (0.52cm^{-1})	5.800 meV (46.79cm^{-1})
2	0.081 meV (0.65cm^{-1})	5.817 meV (46.92cm^{-1})
3	0.117 meV (0.94cm^{-1})	5.854 meV (47.22cm^{-1})
4	0.200 meV (1.61cm^{-1})	5.937 meV (47.89cm^{-1})

^a After Stillman et al.⁸

^b The ionization energies include the deepening of the $1s$ state due to both central cell shifts and conduction band nonparabolicity.

^c The magnitudes of the ionization energies are accurate within about $\pm 0.15\text{cm}^{-1}$, while the differences between the energies are known to about $\pm 0.01\text{cm}^{-1}$.

The photothermal ionization spectroscopy apparatus includes a tunable light source (a spectrometer), a cryostat for controlling the temperature of the sample, and some means for recording the sample's electrical conductivity. The sample temperature is chosen such that without illumination nearly all of the uncompensated donors are occupied by an electron ($kT \leq E_1$). When the light source is turned on, if the photon energy $h\nu \geq E_1$ electrons can be excited directly to the conduction band from their bound donor ground states. These additional carriers increase the conductivity of the sample. In principle, it would be possible to measure central cell corrections by measuring the threshold of such a process, but, in practice, the threshold is not sharp enough to permit this measurement.

Under certain conditions, however, the extrinsic photoconductivity is dominated by a multistep process called excited state photoconductivity, and it is this process through which the central cell corrections are obtained. The mechanism for excited state photoconductivity can be understood by considering an electron in an excited impurity state, having made the transition from the ground state by absorption of a photon. In its subsequent transitions to other states, the electron absorbs or emits phonons. It can jump directly back to the ground state or to the conduction band by emitting or absorbing a phonon of sufficient energy. It can also pass from one bound excited level to another absorbing and emitting phonons, but eventually it will either have made the transition to the conduction band or back to the ground state.

In a photothermal ionization spectroscopy experiment, the temperature is chosen such that there are ample phonons energetic enough to carry an electron from the excited state of interest to the conduction band, and yet few phonons sufficiently energetic to excite electrons from the impurity ground state.

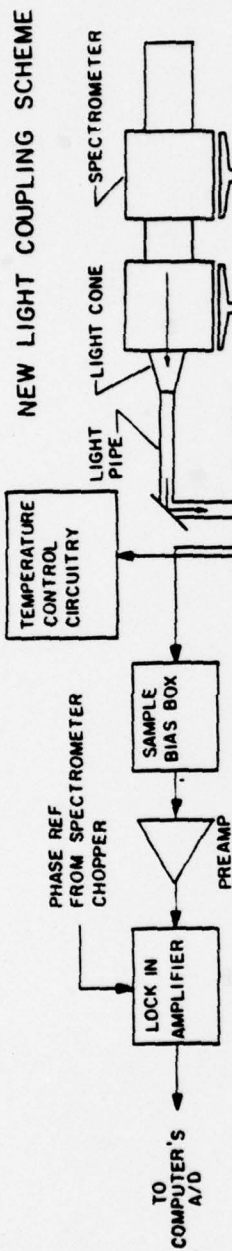
Suppose one is probing the 1s-2p transition. When the light source is tuned through $h\nu = (E_{2p} - E_{1s})$ there is a peak in the electrical conductivity which corresponds to a 1s-2p photon absorption followed by absorption of phonon(s) which carry the impurity electron into the conduction band. In practice this particular transition is of interest since at the appropriate temperature it is the largest peak in the extrinsic photoconductivity spectrum. The 2p state is almost totally unaffected by the central cell correction since the p wavefunction is zero at $r=0$. As a result the 1s-2p transition energy, which is impurity dependent through the 1s central cell correction, can be used as a signature of a given impurity species. Zeeman measurements on the 1s-2p transition allow an effective Rydberg Ry^* to be determined so that the 1s central cell correction can be extracted. Also, these Zeeman measurements produce extremely accurate values of the electron effective mass m^* .

FOURIER TRANSFORM APPARATUS

A block diagram of the apparatus appears in Fig.1. It can be viewed as three interconnecting parts; the spectrometer, the cryostat and the data acquisition system. Because the spectrometer, coupling optics, and cryostat are sensitive to vibrations, they have been mounted on an optical table which in turn rests on a large concrete pillar sunk in the ground (separate from the building's floor vibrations).

Spectrometer. The spectrometer is a Beckman FS720 Michelson interferometer which is used as a high resolution ($\pm 0.06\text{cm}^{-1}$) tunable (5cm^{-1} to 1000cm^{-1})

APPARATUS BLOCK DIAGRAM



OLD LIGHT COUPLING SCHEME

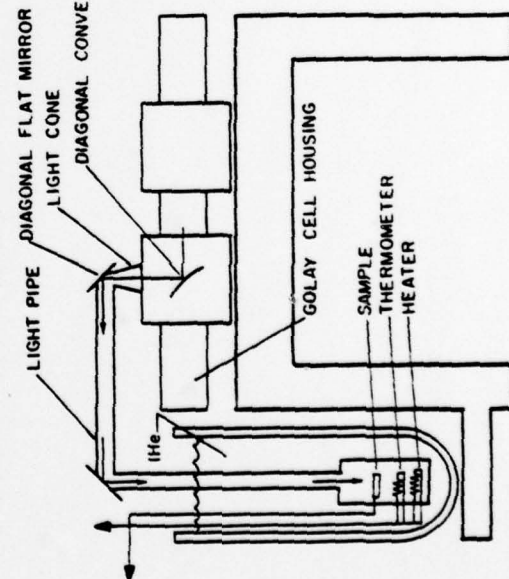


Figure 1.

far infrared (FIR) source for illuminating the semiconductor sample. Light must be coupled out of the spectrometer with suitable optics and guided to the low temperature environment of the sample by means of light pipes. In our first design, a converging beam of FIR light in the spectrometer sample chamber was deflected by a diagonal convex mirror up to a light cone, which coupled to the 45° flat mirrors and light pipes leading to the sample. (See Fig.1.) Alignment problems and loss of light due to astigmatism inherent in the diagonal convex mirror led us to change the coupling optics. This has recently been completed and is pictured in Fig.1. A light cone, positioned at the Golay cell port of the spectrometer sample chamber, attaches directly to the light pipe leading to the sample. The alignment is not critical and essentially all the spectrometer's FIR enters the light pipe at shallow angles. Also this coupling scheme eliminates two diagonal mirrors (their loss being significant in light pipe optics) and permits the use of optical filters built into the spectrometer for removing the strong shorter wavelength components of the radiation which reach the sample. This more efficient coupling of FIR to the sample should increase the overall sensitivity of the apparatus.

Cryostat. There are actually two cryostats, both using the same sample holder insert and coupling in the same way to the spectrometer. Each provides a variable low temperature environment (4.2K-300K or \approx 1.5K-300K if pumped) for the semiconductor sample. This capability is necessary to permit operation at the temperature for the maximum photothermal ionization signal ($T < 4.2\text{K}$ for GaAs, $T < 8\text{K}$ for InP, $4.2\text{K} < T < 10\text{K}$ for Ge, and $23\text{K} < T < 28\text{K}$ for Si). The sample is placed in thermal contact with a large copper mass

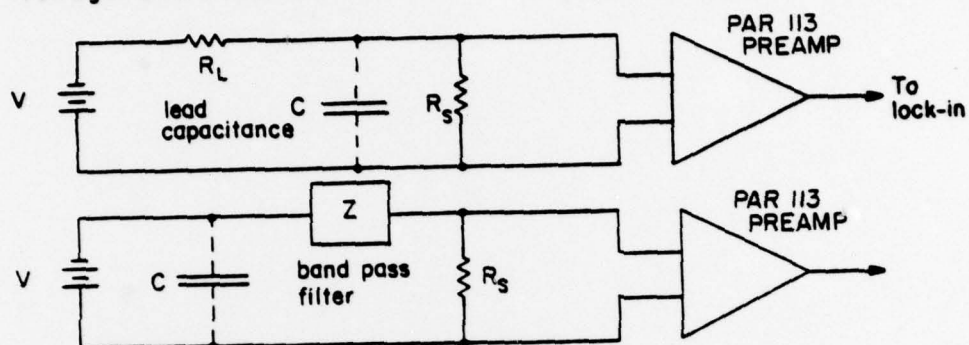
whose temperature is monitored (presently to within ± 1 K) by a carbon resistance thermometer, and controlled by a nonmagnetic resistive heater. In the future, the carbon resistance thermometer will be replaced by a commercial resistance thermometer (either platinum or carbon-glass or both) and a temperature controller will be installed capable of setting and maintaining the temperature to a few millidegrees kelvin. Because the central cell shifts⁶ and the observed line shapes⁷ are magnetic field dependent, it turns out to be easier to resolve the photoconductivity peaks from different impurity species at high magnetic fields. The large Janis Dewar has a superconducting magnet which is capable of providing better than 0.1% spatially uniform magnetic fields up to 60 K Gauss.

The smaller cryostat (2.5 liter liquid He capacity) has been put in operation to allow inexpensive cool-downs for photoconductivity experiments not requiring the magnetic field capability of the large Janis Dewar. It has been designed to achieve liquid He hold times of 6-8 hours which are ample for multiple photoconductivity runs without refilling.

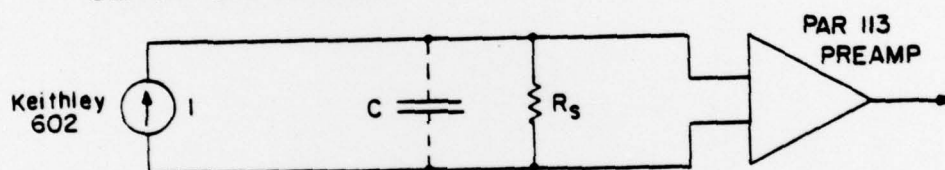
Sample Biasing Electronics. The sample biasing electronics may be in one of at least three configurations (see Fig.2) depending on sample resistance, responsivity, and noise considerations. In each configuration the electric field in the sample is set just below the threshold for impact ionization of the impurities. This threshold is determined from an I-V measurement on the sample and corresponds to a threshold current of $I_t = 0.01-0.1 \mu\text{A}$ in GaAs. With chopped FIR light incident on the sample, a preamplifier then gives a signal at the chopper frequency proportional to the difference in conductivity of the sample with the light on from that with the light off. The amplitude of this signal is measured

SAMPLE BIASING MODES

Voltage Source Mode



Current Source Mode



Current Amplifier Mode

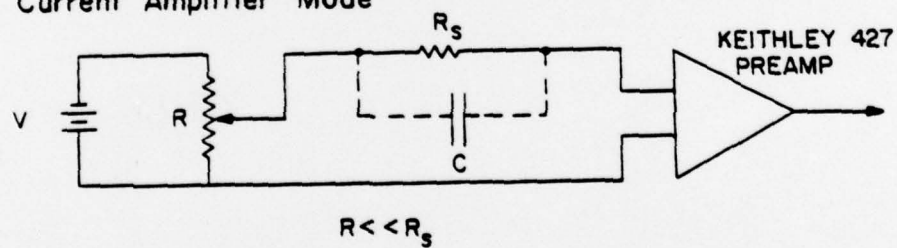


Figure 2.

by a lock-in amplifier referenced with a signal from the chopper, and fed into the data acquisition system as each Δx interval of interferometer mirror position is traversed. At present, the preamplifier output goes to a phase sensitive detector in the analog electronics of the spectrometer, where only low resolution (0.4cm^{-1}) transforms can be performed. In the high resolution measurements the preamplifier output will be read by an Ithaco Model 393 lock-in amplifier which will be coupled through a 12 bit A/D converter to the LSI-11 computer interface (BIN BOX in the Block diagram of Fig.3).

The voltage source mode is currently being used because of the availability of a PAR 113 high input impedance voltage amplifier. For a fixed current the maximum signal is obtained from the sample R_s by letting V and R_L become large (fixing $V/(R_L+R_s) \leq I_c$). Too large an R_L contributes thermal noise $\propto \sqrt{RT}$, which is especially large if R_L is at room temperature (as it presently is). Also, with the necessarily large values of R_L and R_s used difficulties with lead capacitance become pronounced. The stray capacitance C of the leads is charged, and if this capacitance changes (e.g., through vibrations in the insert induced via liquid He boil-off or attached vacuum pumps) in a time $t \leq R_p C$, where R_p is the parallel resistance of R_L and R_s , then a signal of order $(\Delta C/C)V$ will appear across R_s . With the large resistances involved, almost all vibrations of the insert satisfy the above inequality and, as a result, appear as spurious signals. Replacing R_L with a band-pass filter, at the sample end of the leads, which resonates at the chopper frequency, and has a resistive impedance of R_L at this frequency, will improve the signal-to-noise ratio of this configuration.¹ Steps have been taken to minimize insert vibrations, but the lead capacitance problem can be eliminated entirely by switching to a different sample biasing mode.

The current source mode replaces V and R_L with a current source (Keithley Model 602 electrometer) whose current is adjustable in the allowed ranges. Because of the high impedance of the current source, it suffers from the same lead capacitance problem as described above.

We expect the current amplifier mode of operation to turn out to be the most satisfactory. The sample is biased with a low noise voltage source with no load resistor, and the change in current due to chopped illumination is amplified by a Keithley 427 current amplifier. The low impedances of the voltage source and the current amplifier eliminate the lead capacitance difficulties. The Keithley has an excellent noise figure in the range of interest (10^{-13} amp) which gives an estimated S/N of 10^3 in a typical sample.

Data Acquisition System. The functions of this block of the apparatus (see Fig. 3) are to record the electrical conductivity of the semiconductor sample as a function of the Michelson interferometer mirror position and to perform any mathematical preprocessing on this raw data (the interferogram) and then to Fourier transform it, giving the photoconductivity as a function of wavenumber or photon energy (the transformed spectrum). The positions of the peaks and the lineshapes in the transformed spectrum are then interpreted as energy level spectra and impurity interactions. The spectrometer itself has an analog computer to record and Fourier transform the interferogram, but it can perform only low resolution ($\geq 0.4\text{cm}^{-1}$) transforms and can do no preprocessing of the interferogram prior to transforming it. To Fourier transform the interferograms

DATA ACQUISITION SYSTEM BLOCK DIAGRAM

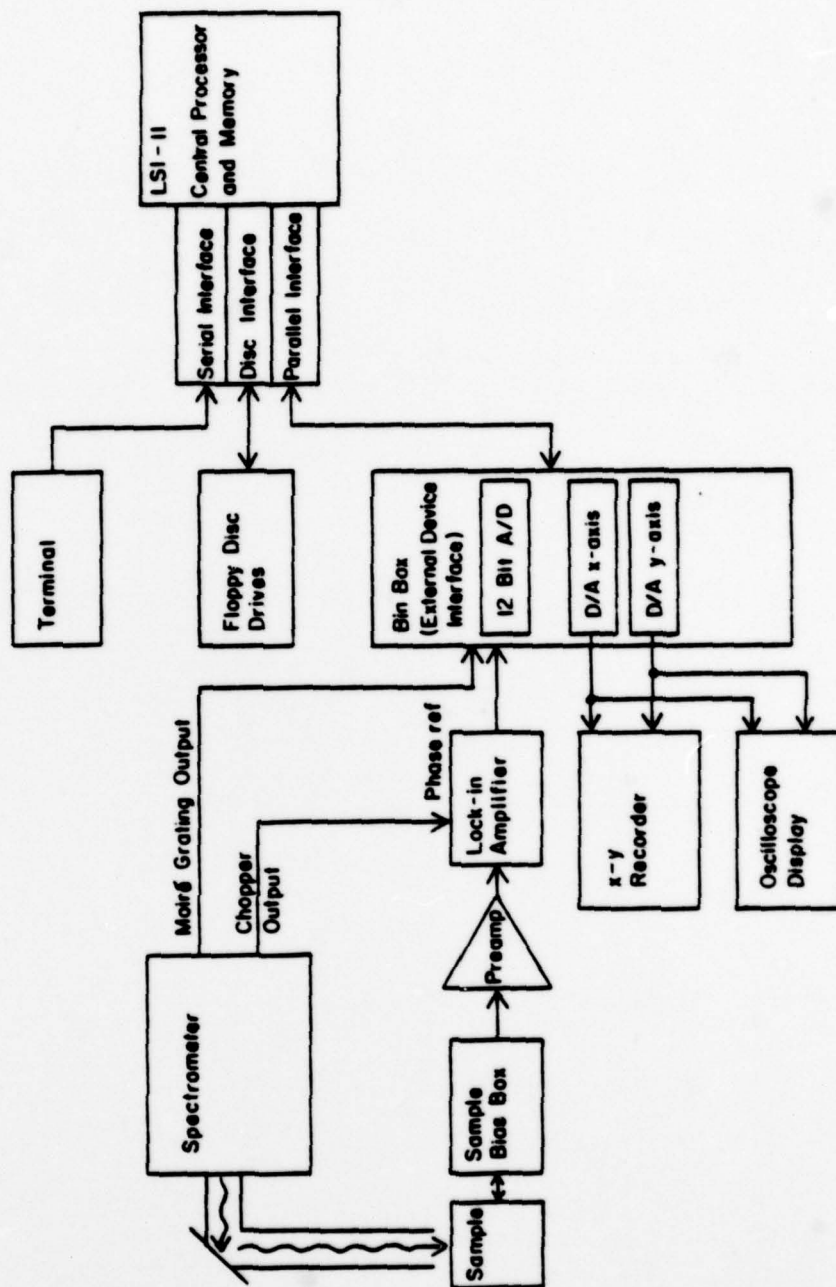


Figure 3.

at the optical resolution limit of the interferometer ($\pm 0.06\text{cm}^{-1}$), we have installed an LSI-11 minicomputer and interface box (BIN box in Fig.3) through which the computer communicates with the experiment. In this configuration, each time the interface box receives a pulse from the Moiré grating electronics in the spectrometer (indicating that a specified Δx in mirror position has been traversed) the LSI-11 will record the lock-in output through an A/D converter as one data point in the interferogram. When a certain predetermined number of data points have been recorded (up to 16,394 but more typically 2048), the completed interferogram can be plotted on the x-y recorder and/or oscilloscope display.

The LSI-11 can also mathematically preprocess the interferogram data prior to performing the Fourier transform, removing noise pulses (which show up as oscillations in the transformed spectrum), removing baseline shift, and apodizing (i.e., smoothly removing the large Δx wings of the interferogram as is often desirable for finite transforms). After the interferogram is transformed, the LSI-11 plots the photoconductivity spectrum on an x-y recorder and/or oscilloscope display, and can be used for curve fitting of the spectral line shapes and for the accurate location of peaks. Both the interferogram and the transformed photoconductivity spectrum are stored on floppy discs for possible future reference.

At present the LSI-11 computer is fully operational and the interfacing to the sample biasing electronics, spectrometer, and display is nearly complete. In the mean time, interferograms are recorded and transformed (at 0.4cm^{-1} resolution) with the spectrometer analog computer.

We have recently finished debugging a FORTRAN IV fast Fourier transform program specifically designed for performing transforms on interferometer

data. It is capable of pretreating the interferogram and performing the phase-corrected, one-sided transforms which are necessary to obtain the ultimate 0.06cm^{-1} resolution from the spectrometer.

Immediate Plans

Dr. P.M. Hemenger of the Air Force Materials Laboratory has provided us with Si samples along with Hall data suggesting the existence of X-levels in these samples. Absorption data have been taken by Scott² on the In and Al X-levels in Si, but the inherent sensitivity of photothermal ionization spectroscopy relative to absorption measurements, especially at low impurity concentrations, should allow us a much closer look at the energy spectra of these levels. Now that the apparatus is operational we will continue looking for the X-levels in Dr. Hemenger's Si samples.

As they become available, we will turn our efforts to the study of InP samples prepared by Professor C.M. Wolfe in St. Louis. There is scant data on the identification of impurities in InP. Stradling et al.^{3,4} have done some measurements on moderately doped n-InP ($N_D - N_A = 2 \times 10^{15} \text{cm}^{-3}$) in a 25 K Gauss magnetic field giving a value for m^* and Ry^* from the Zeeman splitting of the $1s-2p$ transitions. However, it was impossible to resolve chemical shifts due to different donors (owing to the rather large impurity concentrations and the attendant impurity interaction broadening). With the higher quality InP we hope to obtain ($N_D - N_A \leq 1.2 \times 10^{14} \text{cm}^{-3}$ and $\mu_{77} \geq 140,000$), we expect to resolve these chemical shifts. Because of the larger Ry^* in InP (7.65 meV compared to 5.76 meV in GaAs), they are expected to be more easily resolved than in GaAs. Also the smaller Bohr radius associated with impurities in InP should allow sharp line spectra

to be observed at somewhat higher impurity concentrations than in GaAs. By correlating oscillator strengths in the photoconductivity spectra with growth techniques and with controlled (e.g., neutron transmutation) doping, we hope to identify the impurities associated with the individual peaks. The oscillator strength of a given peak is expected to be proportional to the concentration of the associated impurity.

There is now a considerable research effort in many different laboratories, using several different growth techniques, to further refine the control of purity in epitaxial GaAs and to develop the techniques required to produce high-purity epitaxial InP. There have also been significant advances in the preparation of high-purity bulk crystals of GaAs and InP. Some of the techniques currently being studied to obtain high-purity GaAs include, in vapor phase systems, very low temperature growth and growth under different gas composition conditions including high HCl partial pressures, large As/Ga ratios, and the addition of NH_3 to the reactant gases.⁵ The influence of different reactor materials, such as BN liners graphite sample supports, on the purity of the material is also being examined. In liquid phase epitaxial systems, the study of the influence of growth temperature, melt bake-out, and boat material, etc., on purity has received considerable attention.

We plan to study the influence of these various procedures on GaAs and InP grown in our own laboratory, and more importantly, to study the influence of various growth procedures on GaAs and InP crystals prepared in different government, industrial and university laboratories. By

providing this service to other workers who do not have shallow donor spectroscopy capability we should be able to help determine the growth parameters that will result in the lowest total electrically active impurity concentration possible and, in addition, obtain a much better understanding of the source and behavior of residual donor impurities in these materials than would ever be possible by examining only samples grown in one particular laboratory.

Some of our specific objectives are:

- (a) Measure shallow donor spectra of high purity InP and GaAs prepared in various government, industrial and university laboratories.
- (b) Compare the residual donor impurities in samples grown by AsCl_3 and AsH_3 or PCl_3 and PH_3 vapor phase techniques.
- (c) Compare the residual donor impurities in H_2 and N_2 carrier gas vapor phase growth systems.
- (d) Compare the residual donor impurities in liquid and vapor phase epitaxial material.
- (e) Study the variation of relative concentrations of different shallow donors with crystal growth conditions.

As the work progresses, it is anticipated that a joint effort on the intentional doping of high-purity InP prepared using the PCl_3 growth technique will develop with Professor C.M. Wolfe of Washington University. The goal of this interaction will be the identification of the particular chemical species that are the residual donors in unintentionally doped high-purity InP. This work will require close cooperation in the growth,

electrical measurements and far infrared photoconductivity measurements, and it is essential for the actual identification of the residual donor species in high-purity InP.

Possibilities for the Future

The apparatus, through relatively minor modifications, can be an enormously versatile tool for the study of a variety of properties of impurities in semiconductors. Among the many possibilities are:

(1) Line Shape Effects.

- (a) Stark shifts⁶ (0.4cm^{-1} at $4.4 \times 10^{13}\text{cm}^{-3}$ in GaAs) and Stark broadening (full width at half maximum (FWHM) $0.4\text{--}0.8\text{cm}^{-1}$ in $4.4 \times 10^{13}\text{cm}^{-3}$ GaAs). Ionized impurities alter the energy level spectrum of a neutral impurity via their electric field. The distribution of these altered energy spectra forms the line shape of the photoconductivity peak and give information about the distribution and number of ionized impurities in the sample.

By varying the sample growth conditions, sample temperature, sample bias voltage or background illumination, we can control the number of ionized impurities and derive such information from the manner in which the Stark effects change.

- (b) Van der Waal's line shape⁷ (FWHM $0.1\text{--}5\text{cm}^{-1}$): In moderately doped ($\sim 2 \times 10^{15}\text{cm}^{-3}$) uncompensated ($N_I \leq 0.2N_N$) material, the neutral-neutral impurity interaction is expected to become important.³ For a single donor species, this interaction is expected to produce a doublet in the photoconductivity spectrum. For such samples, an understanding of this effect is important if one is interpreting the photoconductivity spectrum chemical shifts in terms of multiple impurity species.

(2) Zeeman splitting

The most precise values of m^* and Ry^* in GaAs have been obtained by examining the $1s-2p$ transition splitting as a function of magnetic fields.⁸ Studies of this effect in pure InP samples have yet to be done.

(3) Stress measurements in polarized light

The light coming from the spectrometer is $\geq 80\%$ polarized. Rotating the plane of polarization with respect to a stress vector in the sample and the sample's crystal axes has given symmetry information with regard to impurity complexes in Si.¹ This technique may well contribute to the identification of impurity species involved in complexes in the III-V's.

REFERENCES

1. A.K. Ramdas and C. Jagannath, Private Communication.
2. W. Scott, Appl. Phys. Lett. 32 (9), 1 May 1978 p.540 C.E. Jones, D.E. Schafer, M.W. Scott, R.J. Hager, Honeywell Inc. Corporate National Science Center Semiannual Report for 1 February to 31 July 1978.
3. J.M. Chamberlain, H.B. Ergun, K.A. Fehring, R.A. Stradling, Solid State Communications V-9 p 1563 (1971).
4. R.A. Stradling, L. Eaves, R.A. Hoult, N. Miura, P.E. Simmonds, and C.C. Bradley, Proc. 1972 Symposium on Gallium Arsenide and Related Compounds (Inst. Phys. Conf. Ser 7, 1973) p.11.
5. G.B. Stringfellow and G. Ham, J. Electrochem. Soc. 124, 1806 (1977).
6. C.M. Larsen, Phys. Rev. B 8, 532 (1973).
7. David M. Larsen Private Communication, (to be published)
8. G.E. Stillman, C.M. Wolfe, J.O. Dimmock, Far-Infrared Photoconductivity in High Purity GaAs in Semiconductors and Semimetals V-12, p.169 (1977) Academic Press.

